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# PROVISIONAL SPECIFICATION.

Communicated by the **FARBENFABRIKEN vormals FRIEDRICH BAYER & COMPANY**, of 217, Koenigstrasse, Elberfeld, in the Empire of Germany, Manufacturers.

## Manufacture and Production of New Diazotizable Dyestuffs.

I, **PAULIP ARTHUR NEWTON**, of 6, Bream's Buildings, Chancery Lane, London, E.C., Chartered Patent Agent, do hereby declare the nature of this invention to be as follows:—

Green substantive dyestuffs capable of being diazotized could hitherto not be obtained, though they are of great technical interest for completing the series of shades and for modifying the shades produced by other dyestuffs capable of being diazotized.

My foreign correspondents have now succeeded in obtaining such dyes capable of dyeing cotton green to blue shades. The process for their production consists in combining diazocompounds of acidyl-para-phenylene-diamines or acidyl-1.4-naphthylenediamines or their derivatives with a suitable middle component which can be further diazotized after the combination. The intermediate compound thus obtained is then rediazotized and combined with 2-amino-8-naphthol-6-sulphonic acid, the resulting colouring matter is rediazotized coupled with methylketol (alpha-methylindol) or a pyrazolone, the trisazo-dyestuffs are finally saponified.

This process can also be performed by using instead of acidyl-para-phenylene-diamines or acidyl-1.4-naphthylenediamines, the corresponding nitrocompounds and by reducing the nitro group contained in the trisazodyestuffs thus obtained.

The new dyestuffs dye cotton in green-blue to green shades, which on being diazotized and developed on the fibre, e.g. with beta-naphthol, produce dyeings very fast to washing and to light, and which can be discharged with hydro-sulphite to a very pure white.

In order to illustrate the new process more fully the following examples are given, the parts being by weight:—

### EXAMPLE A.

230 parts of 1-amino-4-acetylaminobenzene-2-sulphonic acid are dissolved in 7000 parts of water and 55 parts of soda, acidulated with 280 parts of hydrochloric acid and diazotized with 69 parts of sodium nitrite at 15 to 20° C. This diazocompound is combined with a solution of the sodium salt of 245 parts of 1.6-naphthylamine sulphonic acid with the addition of 250 parts of sodium acetate. The copulation is finished after a short stirring. The solution is then acidulated 700 parts of hydrochloric acid of 19° Be. and diazotized with 69 parts of sodium nitrite at 10—15° C. After a stirring for  $\frac{1}{2}$  to 1 hour the diazocompound is formed and allowed to run with the addition of 800 parts of soda into a solution of 261 parts of the sodium salt of 2-amino-8-naphthol-6-sulphonic acid. The coupling is soon finished. The disazodyestuff is separated by the addition of salt and filtered off. It is stirred up with 7000 parts of water, 600 parts of hydrochloric acid are added to the suspension, cooled to 0° and diazotized with 69 parts

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of sodium nitrite. It is stirred until the nitrite reaction has disappeared and the diazocompound is then allowed to run into a solution of 174 parts of phenylmethylpyrazolone in 3000 parts of water and 700 parts of soda, which liquid is heated to 10° C. After a stirring for 1 hour it is heated to 60° C. and the dyestuff is salted out. The paste is then poured on 3000 parts of water, heated to boiling, 1400 parts of soda lye (30 *per cent.* NaOH) are then added to it, boiled for  $\frac{1}{2}$  hour and finally cooled to 60—70° C. When the surplus of soda lye is acidulated with a mineral acid, the saponified dyestuff is filtered off. It is soluble in water with an olive-green colour and dyes cotton directly blue-green. The dyeings on being diazotized and developed with beta-naphthol turn into a bluer shade very fast to washing and to light.

## EXAMPLE B.

Instead of the 1-amino-4-acetylamino-benzene-2-sulphonic acid used in Example A, 245 parts of 2-oxalylamino-4-chloro-5-amino-1-anisol are diazotized in the usual manner and further combined and worked up according to Example A. The dyestuff thus obtained dissolves in water with a blue-green colour and dyes cotton directly blue-green. When diazotized and developed with beta-naphthol green-blue shades are obtained, which possess qualities similar to that of the dyestuffs described in Example A.

## EXAMPLE C.

280 parts of 1-acetylamino-4-aminonaphthalene-6-sulphonic acid are dissolved in 7000 parts of water with the addition of 55 parts of soda. Subsequently the solution is acidulated with 280 parts of hydrochloric acid and is diazotized with 69 parts of sodium nitrite at 15—20° C. The combination with 1.6-naphthylamine sulphonic acid and then with 2-amino-8-naphthol-6-sulphonic acid also the further diazotizing of this intermediate product are carried out according to Example A. A solution of 131 parts of methylketol in 280 parts of hydrochloric acid (19° Be.) is allowed to run slowly to the diazocompound of the intermediate product. After one hour's stirring the solution is heated to 30—40° C. and still stirred for 2 hours at this temperature and the dyestuff is then filtered off. The paste is stirred with 3000 parts of water and 200—300 parts of soda in order to obtain an alkaline reaction of the mass. When boiled, 1400 parts of soda lye (30 *per cent.* NaOH) are added to this mass of reaction, boiled for 10 minutes, further stirred for 15 minutes at 90—95° C., then cooled at 60—70° C., acidulated: the surplus of the soda lye and the separated dyestuff is filtered off. The same dissolves in water with a pure green colour and dyes cotton directly in a green shade. These dyeings, when diazotized and developed with beta-naphthol, become a slightly bluer shade very fast to washing and to light.

## EXAMPLE D.

Instead of the second component of the Example C. namely 1.6-naphthylamine sulphonic acid, 137 parts of cresidine are here used, which are dissolved in dilute hydrochloric acid. The finishing of the dyestuff is similar to that as described in Example C. The dyestuff is soluble in water with a blue-green colour, dyes cotton blue-green and gives, when developed, a dark blue-green shade, with the similar qualities to those described in Example C.

## EXAMPLE E.

Instead of the 1-acetylamino-4-aminonaphthalene-6-sulphonic acid used in Example C, the 1-amino-4-nitronaphthalene 6-sulphonic acid can herein be employed. The couplings are performed in a similar manner as in Example C. The dyestuff, when finished, is likewise stirred with dilute hydrochloric acid, then stirred for several hours with 400 parts of crystalline sodium sulphite at 15—20° C. until the green-blue colour is passed into a pure green. The reduced

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dyestuff is salted out. It is somewhat bluer than that of Example C. The qualities are similar to the above mentioned dyestuffs.

My foreign correspondents do not confine themselves to the particulars given in the above examples which are merely typical and can be varied within wide limits without altering thereby the nature of this invention.

Dated this 9th day of March, 1911.

NEWTON & SON,  
Chartered Patent Agents,  
6, Breau's Buildings, Chancery Lane, London, E.C.,  
Agents for the Applicant.

## COMPLETE SPECIFICATION.

*Manufacture and Production of New Diazotizable Dyestuffs.*

I, PHILIP ARTHUR NEWTON, of 6, Breau's Buildings, Chancery Lane, London, E.C., Chartered Patent Agent, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

My foreign correspondents have now succeeded in preparing new dyes which are capable of dyeing cotton in green to greenish-blue shades. The process for their production consists in combining diazocompounds of acidyl-para-phenylenediamines or of acidyl-1.4-naphthylenediamines or of their derivatives with a suitable middle component which can be further diazotized after the combination. The aminodiazocompounds thus obtained are again diazotized and combined with 2-amino-8-naphthol-6-sulphonic acid; the resulting aminodisazo colouring matters are diazotized, coupled with methylketol (alpha-methylindol) and the trisazodyestuffs thus obtained are finally saponified.

Analogous products are obtained by combining diazocompounds of acidyl-1.4-naphthylenediamines or of their derivatives with a suitable middle component which can be further diazotized after the combination, then diazotizing the aminodiazocompounds thus obtained and combining them after diazotation with 2-amino-8-naphthol-6-sulphonic acid, diazotizing again the resulting aminodisazocompounds and coupling them with a pyrazolone with a free 4 position and finally saponifying the trisazodyestuffs thus produced.

The same results are obtained on using in these processes instead of acidyl-para-phenylenediamines or of acidyl-1.4-naphthylenediamines or of derivatives of these compounds the corresponding nitroaminocompounds and on finally reducing the nitro group contained in the trisazodyestuffs, instead of eliminating the acidyl group contained in the trisazodyestuffs if prepared as before described.

The new dyestuffs dye cotton in green to greenish-blue shades, which on being diazotized and developed on the fibre e.g. with beta-naphthol produce dyeings very fast to washing and to light, and capable of being discharged with hydro-sulphite to a very pure white.

In order to illustrate the new processes more fully the following examples are given, the parts being by weight:—

## EXAMPLE A.

280 parts of 1-acetylamino-4-aminonaphthalene-6-sulphonic acid are dissolved in 7000 parts of water and 55 parts of soda. The solution is acidulated with 280 parts of hydrochloric acid and diazotized with 69 parts of sodium nitrite at from 15 to 20° C. The diazocompound is combined with a solution of 245 parts of the sodium salt of 1.6-naphthylamine sulphonic acid containing 250 parts of

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sodium acetate. The combination is finished after stirring for a short time. The solution is then acidulated with 700 parts of hydrochloric acid of 19° Be. and diazotized with 69 parts of sodium nitrite at from 10—15° C. After stirring for about 1 hour the diazotation is complete and the diazo compound is allowed to run into a solution of 261 parts of the sodium salt of 2-amino-8-naphthol-6-sulphonic acid and 800 parts of soda. The coupling is soon finished. The disazo dyestuff is separated by the addition of salt and filtered off. It is well mixed with 7000 parts of water; 600 parts of hydrochloric acid are added to the paste and the mixture is cooled to 0° and diazotized with 69 parts of sodium nitrite. It is stirred until the nitrite reaction has disappeared and the diazo compound is then allowed to run into a solution kept at a temperature of 10° C. of 174 parts of 1-phenyl-3-methyl-5-pyrazolone in 3000 parts of water and 700 parts of soda. After stirring for 1 hour it is heated to 60° C. and the dyestuff is salted out and filtered. The paste is introduced into 3000 parts of water and the mixture heated to boiling. 1400 parts of soda lye (30 per cent. NaOH) are then added and the boiling is continued for  $\frac{1}{2}$  hour. After cooling to 60 to 70° C. the excess of soda lye is neutralized with a mineral acid and the saponified dyestuff is collected on a filter. It is soluble in water with an olive-green colour and dyes cotton directly in green shades which on being diazotized on the fibre and developed with beta-naphthol turn into a slightly bluer shade of very good fastness to washing and to light.

**EXAMPLE B.**

280 parts of 1-acetylamino-4-aminonaphthalene-6-sulphonic acid are dissolved in 7000 parts of water with the addition of 55 parts of soda. Subsequently the solution is acidulated with 280 parts of hydrochloric acid and is diazotized with 69 parts of sodium nitrite at from 15—20° C. The combination with 1.6-naphthylamine-sulphonic acid and then with 2-amino-8-naphthol-6-sulphonic acid as well as the further diazotation of this intermediate product are carried out as described in Example A. A solution of 131 parts of methylketol in 280 parts of hydrochloric acid (19° Be) is allowed to run slowly into the diazo compound produced from the intermediate product. After one hour's stirring the solution is heated to 30—40° C. and the stirring continued at this temperature for 2 hours and the dyestuff after being salted out is filtered off. The paste is well mixed with 3000 parts of water and 200—300 parts of soda in order to render the mixture throughout alkaline. It is then heated to boiling and 1400 parts of soda lye (30 per cent. NaOH) are added. The boiling is continued for 10 minutes, the mixture is afterwards stirred for 15 minutes at 90—95° C., then cooled to from 60—70° C. acidulated to neutralize the excess of the soda lye and the separated dyestuff is filtered off. It dissolves in water with a pure green colour and dyes cotton directly in green shades, which when diazotized and developed with beta-naphthol turn into slightly bluer shades of excellent fastness to washing and to light.

**EXAMPLE C.**

Instead of the second component of the Example B namely 1.6-naphthylamine sulphonic acid, 137 parts of cresidine dissolved in dilute hydrochloric acid are used. The further operations for the preparation of the dyestuff are similar to those described in Example B. The dyestuff is soluble in water with a bluish-green colour and dyes cotton in bluish-green shades which when developed turn into a dark bluish-green of similar properties to those obtained from the product of Example B.

**EXAMPLE D.**

Instead of the 1-acetylamino-4-aminonaphthalene-6-sulphonic acid used in Example B, the 1-amino-4-nitronaphthalene-6-sulphonic acid is used. The combinations which are the same as in Example B are carried out in a similar manner as there described. The final trisazo dyestuff is likewise well mixed with a dilute

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solution of soda, then stirred for several hours with 400 parts of crystalline sodium sulphide at from 15—20° C. until the greyish-blue colour has changed into a pure green. The reduced dyestuff is salted out. The shades produced from it are somewhat bluer than those of Example B but otherwise of similar properties.

My foreign correspondents do not confine themselves to the particulars given in the above examples which are merely typical and can be varied within wide limits without altering thereby the nature of this invention.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to me from abroad, I declare that what I claim is:—

1. Process for producing new dyestuffs capable of being diazotized, which process consists in combining diazocompounds of acidyl-para-phenylenediamines or of acidyl-1.4-naphthylenediamines or of their derivatives with a suitable middle component which can be further diazotized after the combination, then diazotizing the aminoazocompounds thus obtained and combining them after diazotation with 2-amino-8-naphthol-6-sulphonic acid, diazotizing again the resulting aminodisazocompounds and coupling them with methylketol (alpha-methylindol) and finally saponifying the trisazodyestuffs thus produced, substantially as described.
2. Process for producing new dyestuffs capable of being diazotized, which process consists in combining diazocompounds of acidyl-1.4-naphthylenediamines or of their derivatives with a suitable middle component which can be further diazotized after the combination, then diazotizing the aminoazocompounds thus obtained and combining them after diazotation with 2-amino-8-naphthol-6-sulphonic acid, diazotizing again the resulting amino-disazocompounds and coupling them with a pyrazolone with a free 4-position and finally saponifying the trisazodyestuffs thus produced, substantially as described.
3. Modification of the processes described in Claims 1 and 2, which modification consists in using instead of acidyl-para-phenylenediamines or of acidyl-1.4-naphthylenediamines or of derivatives of these compounds the corresponding nitro-aminocompounds and in finally reducing the nitro group contained in the trisazodyestuffs, substantially as described.
4. As new articles of manufacture the new dyestuffs.

Dated this 28th day of August, 1911.

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